

Comment on “Off-stoichiometry mechanism of the isotope effect in manganites”

In a recent paper, Nagaev [1] cited the unpublished paper by Franck *et al.* to support his theoretical model for the mechanism of the giant isotope effect observed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+y}$ ($x = 0.20$, $y > 0$) [2]. His model suggests that the off-stoichiometric oxygen content depends strongly on the oxygen isotope mass, which leads to a giant oxygen-isotope effect. Here I show that his theoretical model is not consistent with any experimental results (even the results recently published by Franck *et al.* [3]), and his estimate of polaronic bandwidth is wrong due to his misuse of polaronic theories.

Nagaev cited the unpublished data by Franck *et al.* to support his claim. As a matter of fact, Franck *et al.* have discarded the data Nagaev cited, and only published the reliable data which clearly show that the oxygen contents of both isotope samples are the same even if the samples are off-stoichiometric and have a giant oxygen-isotope shift [3]. Actually the giant oxygen-isotope effect for the off-stoichiometric samples ($x = 0.20$, $y > 0$) is due to the fact that the samples are metallic and close to the boundary of the metal-insulator transition. The reduced isotope effect in the stoichiometric samples ($x = 0.20$, $y = 0$) [3] may be tied with the fact that the samples are ferromagnetic insulators at low temperatures [4,5]. The reduced pressure and isotope effects observed in the insulating ferromagnetic phase [6] should be associated with the reduction of the ferromagnetic coupling contributed from charge carriers.

There are other experimental facts which can further argue against the model by Nagaev [1]. According to his argument [1], the isotope effect in more nonstoichiometric samples should be larger. This is in contradiction with experiment. The stoichiometric $(\text{La}_{0.25}\text{Pr}_{0.75})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ shows a very large isotope effect [7], while the very nonstoichiometric $(\text{LaMn})_{0.945}\text{O}_3$ has a rather small isotope effect [8].

If one carefully examines the theoretical calculation in Ref. [1], one will find that the excess oxygen content for the ^{16}O sample should be lower than for the ^{18}O sample by about 4% at temperatures $T > \omega$, where ω is the highest phonon frequency, which is 950 K in LaMnO_3 [9]. Because the oxygen-isotope exchange was carried out at $T > 1200$ K ($> \omega$), and because the oxygen content in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+y}$ remains unchanged below 1000 K ($> \omega$) according to our thermogravimetric analysis, the calculation of Ref. [1] actually suggests that the excess oxygen content y for the ^{16}O sample should be lower than for the ^{18}O sample by about 4%. With $y = 0.02$ (Ref. [4]), one finds that the oxygen content for the ^{16}O sample is lower than for the ^{18}O sample by 0.0008. Thus, the predicted isotope effect is negligibly small and has an

opposite sign as what observed.

His argument against strong electron-phonon coupling in manganites is lack of scientific grounds. Millis *et al.* [10] clearly showed that the double-exchange alone cannot explain the resistivity peak at T_C and thus proposed that strong electron-phonon coupling should be involved to describe the basic physics of the material. The experimental evidence for the strong electron-phonon coupling in manganites is overwhelming [11].

The estimate of the polaronic bandwidth in Ref. [1] is incorrect. Nagaev misuses the small polaron theory, applying the Holstein *nonadiabatic* expression for the polaron bandwidth to the *adiabatic* region of the parameters: the bare bandwidth $W_0 = 1\text{eV}$ and the characteristic phonon frequency $\omega = 0.01\text{eV}$. It is well known [12] that the nonadiabatic expression overestimates the actual bandwidth by many orders of magnitude, if it is applied to a wrong region of parameters. Actually the $\omega = 0.01\text{eV}$ used by Nagaev in his estimate of the polaron bandwidth is inconsistent with the frequency ($\omega \simeq 0.1\text{eV}$) used to justify his theory of the isotope effect in the same paper [1]. With $\omega \simeq 0.1\text{eV}$, and the polaron binding energy $E_p = 0.5\text{eV}$, the polaron bandwidth is not reduced so dramatically, as Nagaev suggests, but only about one order of magnitude, when the right expression is applied [12].

Finally, Nagaev’s claim that small polarons are inevitably localized in the random potential is false. All states of the polaronic band might be localized if the fluctuation energy, F is about 5 times larger than the polaron half-bandwidth, D [13]. Even with the impurity density as high as $n_{im} = 0.3$ per cell, one obtains $F/D \simeq 0.5$ using the polaron mass, $m^* = 10 m_e$. Hence, F/D is about one order of magnitude below the critical ratio for localization of all polaronic states.

Guo-meng Zhao

Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204.

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